



Krám, P., Čuřík, J., Veselovský, F., Myška, O., Hruška, J., Štědráa, V., Jarchovský, T., Buss, H., & Chuman, T. (2017). Hydrochemical fluxes and bedrock chemistry in three contrasting catchments underlain by felsic, mafic and ultramafic rocks. *Procedia Earth and Planetary Science*, 17, 538-541.
<https://doi.org/10.1016/j.proeps.2016.12.136>

Publisher's PDF, also known as Version of record

License (if available):
CC BY-NC-ND

Link to published version (if available):
[10.1016/j.proeps.2016.12.136](https://doi.org/10.1016/j.proeps.2016.12.136)

[Link to publication record in Explore Bristol Research](#)
PDF-document

This is the final published version of the article (version of record). It first appeared online via Science Direct at <https://doi.org/10.1016/j.proeps.2016.12.136> . Please refer to any applicable terms of use of the publisher.

University of Bristol - Explore Bristol Research

General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

15th Water-Rock Interaction International Symposium, WRI-15

Hydrochemical fluxes and bedrock chemistry in three contrasting catchments underlain by felsic, mafic and ultramafic rocks

Pavel Krám^{a,b,1}, Jan Čuřík^{a,b}, František Veselovský^a, Oldřich Myška^{a,b}, Jakub Hruška^{a,b},
Veronika Štědrá^a, Tomáš Jarchovský^c, Heather L. Buss^d, Tomáš Chuman^{a,b}

^aCzech Geological Survey, Klárov 3, 118 21 Prague 1, Czech Republic

^bGlobal Change Research Institute, Academy of Sciences of the Czech Republic, Bělidla 986/4a, 60300 Brno, Czech Republic

^cHlohová 44, 106 00 Prague 10, Czech Republic

^dUniversity of Bristol, School of Earth Sciences, Bristol BS8 1RJ, United Kingdom

Abstract

Bedrock chemistry from three drill cores and fluxes of precipitation, throughfall and runoff from the 2015 water year were examined in three forested catchments in the western Czech Republic. The coefficient of alkalinity of rocks at the granitic (felsic) LYS catchment fall in the low chemical reactivity category. Rocks from the amphibolitic (mafic) NAZ catchment have high reactivity and rocks from the serpentinitic (mostly ultramafic) PLB catchment have high or even very high reactivity. Streamwater fluxes reflected the composition of the underlying bedrock lithologies, especially for magnesium, nickel and chromium at PLB, and for calcium, arsenic and sulfur at NAZ. Streamwater at LYS reflected incomplete neutralization of acidic deposition in the catchment and had mostly negative alkalinity and correspondingly very high fluxes of potentially toxic inorganic monomeric aluminum. Internal cycling of magnesium and calcium in spruce canopy throughfall was influenced by substrate chemistry at PLB and NAZ. About half of streamwater nitrogen left the catchments in the organic form.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the organizing committee of WRI-15

Keywords: granite; amphibolite; serpentinite; Norway spruce; magnesium; coefficient of alkalinity of rocks

1. Introduction

Chemical weathering of rocks and soils buffers terrestrial and freshwater ecosystems from anthropogenic acidification. The focus of this contribution is to compare bedrock chemistry and hydrochemical fluxes in three

* Corresponding author. Tel.: +420-251-085-432 ; fax: +420-251-818-748 .

E-mail address: pavel.kram@geology.cz

different Czech catchments with substrates that can serve as examples of differing catchment vulnerability to anthropogenic acidification.

2. Study area and methods

The study catchments are situated 5–7 km apart in the Slavkov Forest, western Bohemia, Czech Republic and are forested mainly by even-aged stands of Norway spruce (*Picea abies*). They have similar areas, altitude, annual mean air temperature (5–6 °C), and atmospheric deposition but geochemically differing bedrocks and soils (Tab. 1). Lysina (LYS) and Pluhův Bor (PLB) are in the Czech GEOMON network of catchments and in the international ecological network (ILTER). Moreover, LYS is part of two International Cooperative Programs (ICP) – Integrated Monitoring and Waters. All three catchments formed the Slavkov Forest CZO¹ in 2010, one of the main Critical Zone Observatories of the former European SoilTrEC project.

Table 1. Characteristics of the three study catchments in the Slavkov Forest. Most of the data are from², except for the forested area for 2015 from³ and the biomass growth based on data from^{4,5} and recalculated for 2015.

Catchment	Area (km ²)	Altitude (masl)	Prevailing rock	Prevailing soil	Closed-canopy forest ³ (%)	Spruce (%)	Age (yrs)	Above-ground biomass (t/ha)	Above-ground biom. growth ^{4,5} (t/ha/yr)
Lysina	0.273	829-949	Granite	Podzol	98	100	42	101	4.9
Na Zeleném	0.55	736-802	Amphibolite	Cambisol	89	97	97	277	6.4
Pluhův Bor	0.216	690-804	Serpentinite	Stagnosol	81	88	114	169	0.84

Stream water discharge has been monitored using V-notch weirs and mechanical water level recorders since the 1990 water year (November–October) at LYS, since the 1992 water year at PLB and by a pressure recorder since 2015 at Na Zeleném (NAZ). Stream water was collected at regular intervals (weekly at LYS and PLB and monthly at NAZ) for chemical analysis at these three sites over the last 6 years. Weekly samples or older data were not evaluated for this contribution. Bulk precipitation and canopy throughfall were collected monthly (in total) by 6 and 25 collectors, respectively. Water analyses performed in the Czech Geological Survey (CGS) using standard laboratory methods, which were described previously in detail². Aluminum fractions were measured using colorimetry and cation exchange resin⁶. Calculations of element fluxes in precipitation and throughfall in the 2015 water year were based on 12 samples of each, and runoff calculations were based on 13 samples from each catchment. Rock samples from boreholes drilled to 26–30 m depth in September 2012 were processed and their elemental content was analyzed mostly by FAAS or RFA, also in the accredited CGS laboratories. Sulfur was analyzed by combustion on an elemental analyzer (ELTRA). The coefficient of alkalinity for the rocks was calculated (Eq. 1)^{7,8} using individual concentrations (mol kg⁻¹).

$$Calk = \frac{Na + K + Li + Ca + Mg + Ba + Sr}{Si + Ti + Al + Fe + Mn + Na + K + Li + Ca + Mg + Ba + Sr} \quad (1)$$

3. Results and discussion

All eight analyzed rock core samples from LYS are felsic (with SiO₂ > 65%), with individual contents from 65.4 to 74.7% of SiO₂. Of nine NAZ rock samples analysed, seven are mafic (SiO₂ 45–55%), and two are ultramafic (43–44%). Drill core samples from PLB are the most diverse: of fourteen samples analysed, six are ultramafic (SiO₂ < 45%), with SiO₂ contents from 37.7 to 43.7%, five samples are mafic, and three samples contain 55–58% SiO₂ which correspond to the intermediate category^{9,10}. The largest content of MgO (38.7%) and Ni (0.1%) was detected in the uppermost serpentinite (Fig. 1a) and, naturally, this sample also contains the lowest contents of K₂O and CaO (just 0.01% and 0.04%), as a typical feature of the ultramafic rock. Relatively large concentrations of sulfur (Fig. 1b) were detected at NAZ (up to 0.63%), perhaps partially in the form of arsenopyrite related to elevated concentrations of total arsenic in bedrock (up to 77 ppm). Coefficient of alkalinity values at LYS fall in the low reactivity category (0.1–0.2), whereas almost all values from NAZ and two thirds of values from PLB fall in the high reactivity category (0.25–0.4). Five rock core samples from PLB fall in the very high reactivity category (>0.4), with the highest recorded value (0.56) in the uppermost serpentinite.

Streamwater chemistry at LYS, NAZ and PLB reflected composition of the underlying substrates². Strikingly different concentrations of Mg are shown in Fig. 2a, the high concentrations were recorded only during baseflow, lower values during high flow.

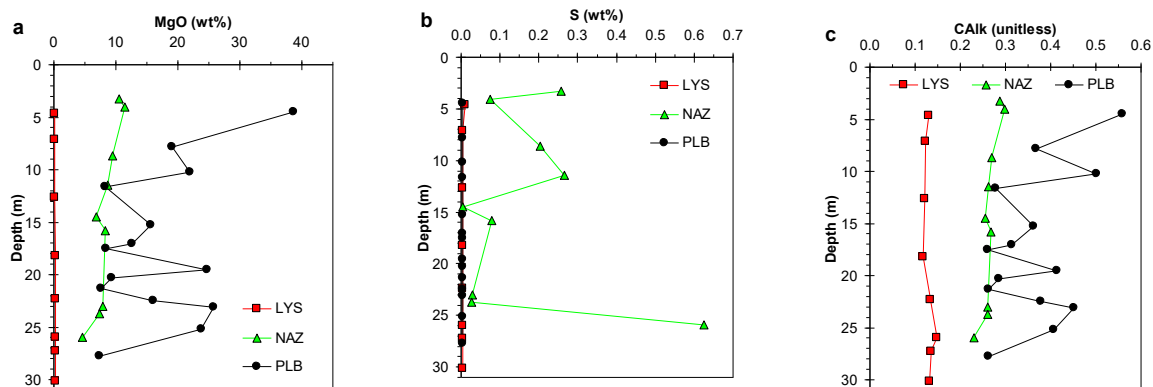


Fig. 1. Chemical composition of rock samples (weight percents) from the drill cores at Lysina (LYS), Na Zeleném (NAZ) and Pluhův Bor (PLB) for (a) magnesium; (b) sulfur; (c) coefficient of alkanity according to Equation 1.

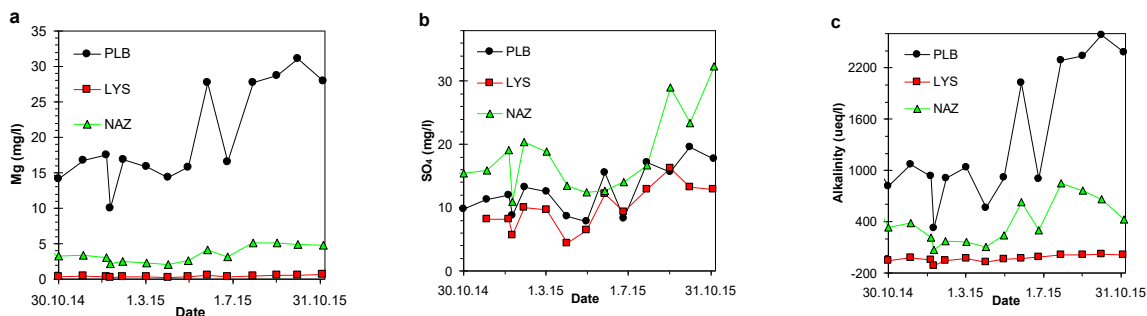


Fig. 2. Streamwater concentrations at Lysina (LYS), Na Zeleném (NAZ) and Pluhův Bor (PLB) in the water year 2015 for (a) magnesium; (b) sulfate; (c) Gran titration alkalinity.

Higher concentrations of sulfate at NAZ (Fig. 2b) probably reflected significant content of S in bedrock at NAZ (Fig. 1b). The strongly anthropogenically acidified streamwater at LYS reflected incomplete neutralization of acidic atmospheric deposition and had chronically low streamwater alkalinity (Fig. 2c) and pH¹¹ (not shown), especially during high flow periods. Precipitation and throughfall fluxes in the 2015 water year reflect the recent reduction in atmospheric deposition of pollutants in Central Europe¹². Total deposition of S calculated from the precipitation and throughfall fluxes (Tab. 2) and the forest cover of catchments (Tab. 1) was 3.7, 5.1 and 4.8 kg ha⁻¹ yr⁻¹ at LYS, NAZ and PLB, respectively. Corresponding net loss of S was 0.7 kg ha⁻¹ yr⁻¹ at LYS and PLB and 1.3 kg ha⁻¹ yr⁻¹ at NAZ which could reflect that approximately half of the S output at NAZ was from internal sources (Fig. 1b). Dry deposition and internal cycling of nutrient base cations were estimated proportionally to Na flux, assuming negligible internal vegetation flux of Na¹³. Throughfall fluxes reflected substrate chemistry, e.g., the largest internal cycling of Mg (84% of the throughfall flux) was calculated at PLB and the largest internal cycling of Ca (74%) was calculated for NAZ and correspondingly the lowest (22%) for LYS. Runoff fluxes (Tab. 2) of elements like Mg, Ni and Cr strongly reflected the composition of the underlying substrates^{2,9,10} (Fig. 1). Comparable output of phosphorus at LYS and PLB (Tab. 2) is surprising because mean P concentrations in granite at LYS⁹ are 5.7 times larger than mean P content in bedrock at PLB¹⁰, where spruce trees suffer P deficiency¹⁴. Perhaps extremely slow above-ground biomass growth of trees at PLB (Tab. 1) and corresponding limited net tree uptake of P are partially

responsible for that situation. About half of runoff N left all three catchments in the form of DON. Incomplete neutralization of incoming acidity at LYS, acidity generation from previously stored S and production of organic acids, caused higher H^+ output flux than input flux (Tab. 2). This acidic environment caused a large runoff output of potentially toxic inorganic monomeric Al (Ali)⁶ at LYS.

Table 2. Open area bulk precipitation fluxes, canopy throughfall fluxes and streamwater fluxes of selected elements and compounds at the three study catchments for the 2015 water year (Nov. 2014 – Oct. 2015). Ali = inorganic monomeric Al (potentially toxic species⁶), Alo = organic monomeric Al, Alp = particulate Al, DIN = dissolved inorganic N (sum of NO_3^- -N and NH_4^+ -N), DON = dissolv. organic N, nd = not determined.

Elem.	Unit	LYSINA			NA ZELENÉM			PLUHŮV BOR		
		Precip.	Through.	Runoff	Precip.	Through.	Runoff	Precip.	Through.	Runoff
Mg	kg ha ⁻¹ yr ⁻¹	0.31	1.0	0.53	0.30	1.9	3.42	0.33	4.2	21.71
Ca	kg ha ⁻¹ yr ⁻¹	2.0	3.0	2.1	1.3	5.4	6.74	1.3	6.4	2.14
K	kg ha ⁻¹ yr ⁻¹	1.7	12.2	0.60	2.2	14.6	1.06	1.7	9.1	0.46
Na	kg ha ⁻¹ yr ⁻¹	1.6	1.9	3.45	1.2	2.9	4.58	1.2	2.3	1.54
Si	kg ha ⁻¹ yr ⁻¹	nd	nd	12.4	nd	nd	10.2	nd	nd	20.9
P	g ha ⁻¹ yr ⁻¹	298	406	160	308	206	71	373	216	151
Ali	g ha ⁻¹ yr ⁻¹	nd	nd	462	nd	nd	8.5	nd	nd	12.3
Alo	g ha ⁻¹ yr ⁻¹	nd	nd	935	nd	nd	219	nd	nd	322
Alp	g ha ⁻¹ yr ⁻¹	nd	nd	1376	nd	nd	581	nd	nd	1954
Ni	g ha ⁻¹ yr ⁻¹	27.1	4.8	2.3	5.0	3.3	3.2	5.2	13.9	265.2
Cr	g ha ⁻¹ yr ⁻¹	2.4	1.10	1.9	1.1	0.76	1.8	1.3	0.99	60.7
F	g ha ⁻¹ yr ⁻¹	110	89	310	71	71	110	77	79	150
S	kg ha ⁻¹ yr ⁻¹	1.8	3.7	4.4	1.3	5.6	6.4	1.5	5.6	5.5
DIN	kg ha ⁻¹ yr ⁻¹	5.30	3.7	0.56	3.82	10.5	0.73	4.46	9.5	1.63
DON	kg ha ⁻¹ yr ⁻¹	0.0	1.6	0.55	0.2	3.2	0.68	0.1	3.4	1.67
DOC	kg ha ⁻¹ yr ⁻¹	12.6	50.0	58.4	11.3	65.9	20.3	11.0	64.6	72.1
H ⁺	g ha ⁻¹ yr ⁻¹	77.3	66.0	222.4	69.7	65.2	1.0	69.9	63.0	0.3

Acknowledgements

This research was supported by projects FP7 244118 (SoilTrEC), CGS 338100, EHP-CZ02-OV-1-020-2014 and GACR 15-08124S. Technical help of V. Kmínek, J. Václavěk (local volunteers) and co-operators from the CGS (V. Bláha, V. Chlupáčeková, F. Oulehle, M. Novák) is acknowledged. **References**

- Regelink IC, Stoof CR, Rousseva S, Weng L, Lair GJ, Kram P, Nikolaidis NP, Kercheva M, Banwart S, Comans RNJ. Linkages between aggregate formation, porosity and soil chemical properties. *Geoderma* 2015;**247-248**:24–37.
- Krám, P, Hruška J, Shanley JB. Streamwater chemistry in three contrasting monolithologic catchments. *Appl Geochem* 2012;**27**:1854–63.
- Orthophoto of the Czech Republic. Czech Office for Surveying, Mapping and Cadastre; 2015.
- Pavloňová G, Cichra D, Hanychová M, Nikl M. Biomass balance for the fourteen GEOMON catchments. Research Report (in Czech). Forest Management Institute UHUL, Brandýs nad Labem, Czech Republic; 2008.
- Černý M, Pařez J, Malík Z. Growth and mensuration tables of the main tree species of the Czech Republic (spruce, pine, beech, oak) (In Czech, English summary). IFER, Institute for Forest Ecosystems Research, Ltd., Jílové u Prahy, Czech Republic; 1996.
- Driscoll CT, Postek KM. The chemistry of aluminum in surface waters. In Sposito G, editor, *The environmental chemistry of aluminum*. Boca Raton, FL, USA: CRC Press; 1995. p. 363–418.
- Adamová M. Geochemical reactivity of rocks – Important environmental factor (in Czech). *Geol Průzkum* 1991;**5**:139–140.
- Chuman T, Gürtlerová P, Hruška J, Adamová M. Geochemical reactivity of rocks of the Czech Republic. *J Maps* 2014;**10**:341–9.
- Štědrá V, Jarchovský T, Krám P. Lithium-rich granite in the Lysina-V1 borehole in the southern part of the Slavkov Forest, western Bohemia (in Czech, extended English abstract). *Geosci Res Rep* 2016;**49**:137–42.
- Štědrá V, Krám P, Farkaš J. Petrology and whole-rock geochemistry of metabasites from borehole cores in the Na Zeleném and Pluhův Bor catchments in the Slavkov Forest, western Bohemia (in Czech, extended English abstract). *Geosci Res Rep for 2014,2015*;103–8.
- Krám P, Farkaš J, Pereponova A, Nwaogu C, Štědrá V, Hruška J. Bedrock weathering and stream water chemistry in felsic and ultramafic forest catchments. *Procedia Earth Planetary Sci* 2014;**10**:52–5.
- Vuorenmaa J, Kleemola S, Forsius M, Lundin L et al. Sulphur and nitrogen input-output budgets at ICP Integrated Monitoring sites in Europe in 1990–2012. *Reports of the Finnish Environment Institute* 2014;**23**:28–34.
- Bredemeier M. Forest canopy transformation of atmospheric deposition. *Water Air Soil Poll* 1988;**40**:121–35.
- Rosenstock NP, Berner C, Smits MM, Krám P, Wallander H. The role of phosphorus, magnesium, and potassium availability in soil fungal exploration. *New Phytol* 2016;**211**:542–53.